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The Reactions of the Ziervogel Process

and

Their Temperature Limits.

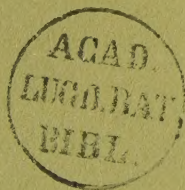
BY

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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR  
THE DEGREE OF DOCTOR OF PHILOSOPHY, IN THE FACULTY  
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MAY, 1902.



NEW YORK CITY:

1902.





## ACKNOWLEDGMENT.

THIS investigation was undertaken at the suggestion of Prof. Henry M. Howe, of the Department of Metallurgy, Columbia University, who, in a letter to the author, dated October 23, 1900, wrote as follows, suggesting the subject of this dissertation :

"The extraction of silver from copper mattes by either the Ziervogel or the Augustin process depends upon converting the silver into silver sulphate by means of the sulphuric anhydride evolved from the decomposition of ferrous sulphate and cupric sulphate, which are formed during the roasting operation itself from the iron and copper sulphides present.

"It occurred to me, some time prior to the autumn of 1897, that these processes might be made much easier by adding to them, at the proper stage, ferrous or cupric sulphate, or both, in the form of green or blue vitriol. That is, instead of having to rely solely on our ability to generate these sulphates in this very delicate roasting operation, my idea was that we could add a small quantity of already-prepared sulphate at the proper state of roasting, viz., at or before the period when the sulphatizing of the silver occurs.

"Besides iron and copper sulphates, I have also thought of the addition of alkaline sulphates for the same purpose, especially of sodium sulphate, which has been used for sulphatizing copper in roasting.

"It seems to me that the Ziervogel process, either alone or jointly with the Augustin process, would form a very useful and interesting subject for your thesis, especially if studied with a view to determining the ranges of temperature and other conditions most favorable to the formation, and those which cause the decomposition, of ferrous, cupric and silver sulphates respectively ; including in your investigation this idea of facilitating the sulphatization of the silver by the addition of green or blue vitriol or sodium sulphate, or two or all of them.

"In doing this I should like it distinctly understood that the work is to be done purely for the advancement of science, and that, if any useful result is reached by the experiments, it is not to be patented by either of us, but is to be published at once for public benefit."

To Prof. Howe the author would express the deepest gratitude for the constant interest he has taken in the progress of the work, and for the valuable counsel he has given on lines of investigation.

R. H. B.

METALLURGICAL LABORATORY,  
HAVEMEYER HALL, COLUMBIA UNIVERSITY,  
May 1, 1902.



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## The Reactions of the Ziervogel Process and Their Temperature-Limits.\*

BY ROBERT HENRY BRADFORD, B.S., UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH.

### THE ZIERVOGEL PROCESS.

The Ziervogel process was invented in 1840† by Hüttenmeister Ziervogel, of the Gottesbelohnungshütte, and was first brought into use in 1844, at Mansfeld, Prussia, by its inventor. Since that time it has been applied more or less continuously at Mansfeld, and at various other places in Europe and in this country, for extracting silver from copper-mattes.

This very simple, though delicate, process depends upon the fact that the silver in copper-mattes is converted into silver sulphate by means of the sulphuric anhydride evolved from the decomposition of iron sulphate and copper sulphate, which are formed during the roasting operation from the iron and copper sulphides present in the mattes. The process consists in roasting the sulphides in excess of air, so that they are oxidized partly to sulphates, which are then heated sufficiently to decompose the sulphates of iron and most of the sulphates of copper, while the silver remains sulphatized, and may be dissolved out with boiling-water and subsequently precipitated on metallic copper. Simple as it appears, this process is extremely difficult to execute, for it requires a very high degree of skill to seize the exact period when the iron and copper sulphates are converted into their insoluble higher oxides and none of the silver sulphate is decomposed.

### OBJECT OF THIS INVESTIGATION.

This investigation was undertaken with the view (1) to determining the conditions most favorable to the formation and those which cause the decomposition of the sulphates of iron,

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\* This paper was submitted as a thesis for the degree of Doctor of Philosophy at Columbia University, New York City; and at the same time accepted by the American Institute of Mining Engineers for publication in the *Transactions* of that Society.

† Lamborn, *Metallurgy of Copper*, p. 147.



copper and silver respectively; and (2) to finding out if these processes might not be made much easier by adding at the proper stage ferrous or cupric sulphate or an alkaline sulphate. Instead of having to rely solely on our ability to generate and control the sulphates in this very delicate roasting operation, could we not add a small quantity of some sulphate at the proper stage of the process, and thereby get the desired results?

#### STEINBECK'S EXPERIMENTS.

Steinbeck,\* in 1862, carried out a series of most valuable experiments on the chemistry of the Ziervogel process as then operated at Mansfeld; and his dissertation is to this day considered classic. He attempted to ascertain approximately the temperature at the various stages of the operation, but the lack of suitable means for accurately measuring high temperatures made it impossible for him to get reliable results. To show the limitations under which he worked, I quote from Steinbeck:† “Lacking a pyrometer, with the help of which high temperatures could be determined with certainty, I contented myself in approximately determining the temperature of the heating charge by means of metals with well-known melting-points. These were exposed continuously for 5 to 5½ hours during the roast in the upper hearth in a spoon 2'' x 2'', made of sheet-iron. By means of a cover made of a non-conducting substance, the heat from the gases near the arch of the furnace was kept out. The cover was made of two concave pieces of porcelain placed together, with their concave sides toward each other and with wood-ashes between them, the two parts being held together by wire. The fusion was thus accomplished through the temperature of the roasting mass, as the crucible was continuously moved back and forth in the roasting-material.” Table I. gives the metals and their melting-points used by Steinbeck, and also the melting-points as determined by the use of improved pyrometers.

With some of the metals no grave difference is noticed on

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\* *Chemisch-Analytische Untersuchungen über die Veränderungen, welche der Mansfelder Kupferstein bei seiner Röstung behufs Eutsilberung durch die Ziervoglsche Extractionsmethode erleidet.* Dr. G. V. A. Steinbeck; also, *Zeitschrift für das Berg-, Hütten, und Salinenwesen in dem Preussischen Staate*, vol. xi., No. 2, p. 95.

† *Chemisch-Analytische Untersuchungen*, etc., p. 48.

TABLE I.—*Melting-Points.*

|                                    | Tin.    | Bismuth. | Lead.   | Zinc.   | Antimony. |
|------------------------------------|---------|----------|---------|---------|-----------|
| Used by Steinbeck.....             | 235° C. | 270° C.  | 334° C. | 412° C. | 425° C.   |
| Obtained with improved pyrometers* | 232° C. | 269° C.  | 327° C. | 420° C. | 630° C.   |

comparing the melting-points employed in his experiments with those recently determined; but in the case of antimony the error is seen to be more than two hundred degrees. Having adopted so low a melting-point for antimony, Steinbeck was led to erroneous conclusions as to the temperature in various stages of the roasting operation, as instanced by the following statements: "At the expiration of one hour and fifteen minutes the entire roast was of a dull-red color; yet it was not able to melt antimony (425° C.), while zinc melted readily. Also, at the last stage of the roast in the upper hearth, antimony was not fused; after three hours roasting, and after keeping the pan one-half hour in the roasting mass, antimony was still brittle, and could be broken with the pincers, and no trace of fusion was perceivable. On the other hand, zinc could be readily melted to the last moment the matte remained in the upper hearth. From these results, it follows that the temperature which the roast attains in the upper hearth lies between the melting-point of zinc and antimony, and consequently cannot rise above 425° C."

Undoubtedly the temperature had risen above 600° C. during the roasting in the upper hearth, instead of remaining below 425° C.; for the temperature of "dull red" referred to is given as 550–625° C. by Prof. H. M. Howe,† and 566°–635° C. by White and Taylor.‡ Concerning the higher temperatures in the lower hearth, he says: "After the mass had been in the lower hearth, whose arched ceiling and side-walls glowed with a bright-red heat from the 'Feuerungsperiod' of shortly before, for ten minutes, antimony (425° C.) was easily brought to fusion. This temperature was greatly exceeded with the roasting mass, but could

\* Le Chatelier and Boudouard, *Mesure des Températures élevées*, p. 11. Also, *High Temperature Measurements* (a translation of the above by Burgess), p. 208.

† H. M. Howe, *Eng. and Min. Jour.*, Jan. 20, 1900, p. 75.

‡ *Am. Soc. of Mech. Engineers*, Dec., 1899, or *Eng. and Min. Jour.*, Dec. 23 1899.



not be determined, even approximately, for want of metals or alloys with suitable melting-points, but allow it to be approximately estimated at  $500^{\circ}$  to  $550^{\circ}$  C." He found that, when antimony was first melted, dehydrated copper sulphate placed in a closed crucible was not decomposed, but retained its white color. Later, this sulphate was decomposed readily on the side of the hearth next the fire.

#### APPARATUS EMPLOYED IN THE PRESENT EXPERIMENTS.

The improvements in pyrometry of the last few years have made it possible to determine accurately the temperature at any stage of the roasting process. The pyrometer employed in this investigation was the Le Chatelier thermo-electric couple, connected up with a d'Arsonval galvanometer mounted on a stone slab arranged on brackets against the wall of the laboratory. The telescope with graduated scale was mounted on the same slab, two meters distant from the galvanometer. The accuracy of this type of pyrometer at high temperatures, and its adaptability for use with small quantities of the substance heated, made it especially applicable to the work in hand.

The Howe electric furnace\* used in this investigation was of inestimable value in many of the experiments. It furnished a means of controlling perfectly the temperatures of the heated substances. The material under treatment could be held at a definite temperature for an unlimited time simply by keeping the current through the furnace constant. The rheostats employed in connection with the furnace are described below. Fig. 1 represents the furnace with crucibles, pyrometer couple, and substance under investigation in place; and all parts are shown in actual size. The body of the furnace was made up of two hemi-cylindrical blocks of magnesium oxid which, when placed together, formed a cylinder with a cup-shaped depression extending from the upper side. Inside of this depression the cylinder was grooved spirally. The platinum wires (two No. 18 Browne & Sharp gauge, twisted together) were wound into a spiral to fit this groove. Inside this spiral of heating-wire was placed the magnesium oxid crucible. Two shoulders forming an

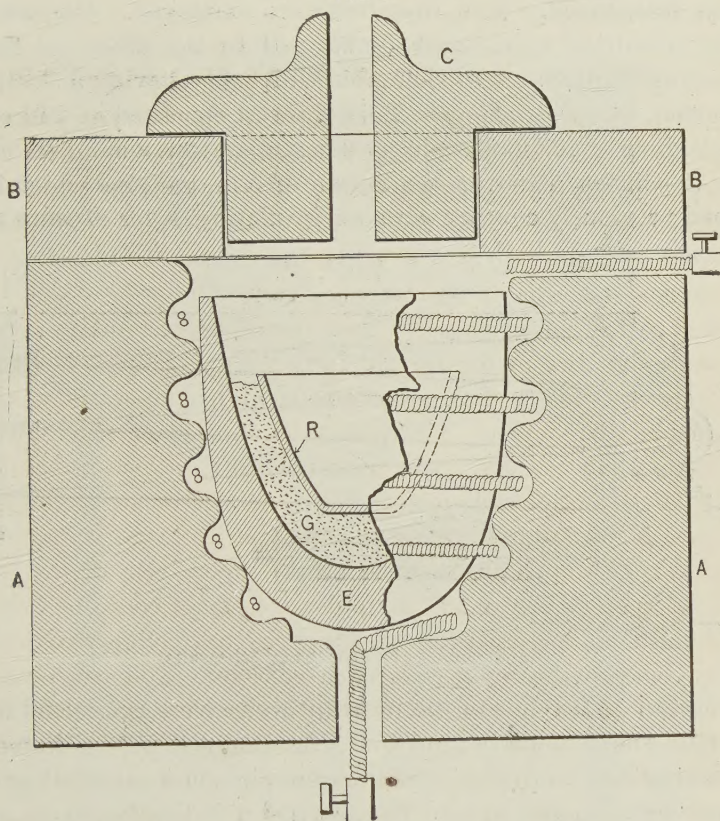
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\* "An Electric Resistance Magnesia Crucible-Furnace for Laboratory Use," by Dr. H. M. Howe, *Eng. and Min. Jour.*, Nov. 16, 1901, p. 636. Paper read before the American Institute of Mining Engineers, Mexican Meeting, 1901.



annular ring around the top of the furnace supported the cap or stopper. The pyrometer couple passed through the cap to the crucibles below. The furnace-body and auxiliary parts were of magnesium oxid. Powdered magnesium oxid formed the bed in which the inner platinum or porcelain crucible was placed.

FIG. 1.



Howe's Electric Resistance Magnesia Crucible-Furnace.

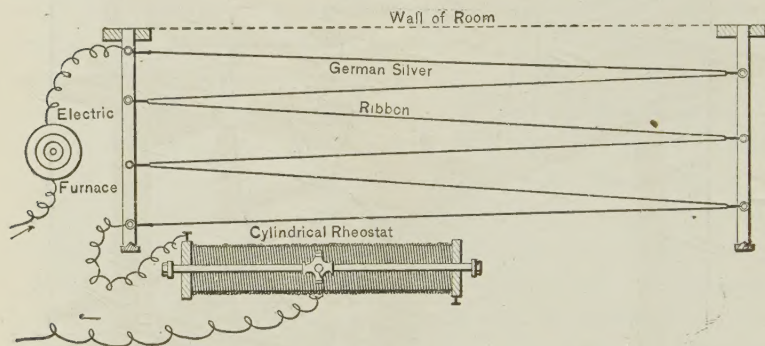
A, Magnesia furnace-body ; B, Magnesia shoulders ; C, Magnesia cap or stopper ; E, Magnesia crucible ; R, Powdered magnesia ; G, Interior porcelain crucible.

The resistance of the furnace-wires varied with the temperature, ranging from 0.13 ohms at ordinary temperature of the room to 0.35 ohms at  $1200^{\circ}\text{C}$ . To maintain a temperature of  $700^{\circ}\text{C}$ . required a current of 27 amperes, while for  $1000^{\circ}\text{C}$ . a current of 32 amperes was necessary. The electric furnace was used almost every day, for a period of six months, without any ap-

parent deterioration of the platinum wire, the outer walls, or the inner crucible.

The current was obtained from the direct-current dynamo which supplied the electricity for general use through the buildings of the University. The voltage (115) was much higher than required by the furnace, so additional resistance was introduced. Two rheostats were employed. One was of the cylindrical type designed and used by the Electrical Engineering Department of Columbia University, having a shifting-contact, to furnish steps. This rheostat consisted of 240 coils of "climax" resistance-wire of 3 mm. diameter, wound six coils to the linear inch around a length of 5-in. gas-pipe which had been previously covered with an insulating layer of mica and

FIG. 2.



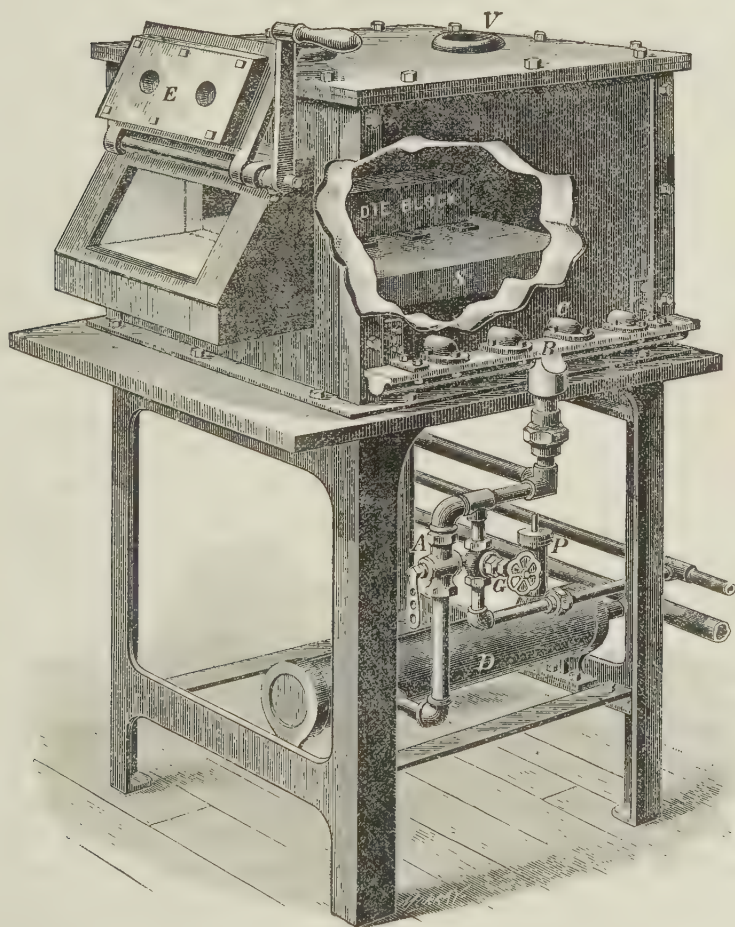
Arrangement of Furnace and Rheostats.

asbestos. The ends of the resistance-wire were connected with binding-posts suitably insulated. An iron rod of  $\frac{3}{4}$ -in. diameter running longitudinally above the gas-pipe, and attached to the same by a support at each end, carried a sliding-brush in contact with the coils of the rheostat and with a binding-post above. The whole was mounted on four legs, and stood a few inches from the floor. The maximum resistance of this one was 0.8 ohms at the temperature of the room. In connection with the necessary additional constant resistance, this rheostat with sliding contact was used to adjust the temperature between the limits employed. The additional constant resistance was supplied by 72 ft. of German silver ribbon, 0.5" wide by 0.008 thick, strung back and forth from cross-pieces, 12 ft. apart, erected along the wall above the furnace. At one



cross-piece each end of the ribbon and each fold was connected by a large copper wire to its binding-post in the cross-piece. Adjustments could easily be made so that two, or four, or six of these lengths were in the circuit. With a current of 40 amperes, the ribbon did not attain a temperature of visible

FIG. 3.



Gas Oven-Furnace.

redness, and did not oxidize to any extent. This simple and inexpensive rheostat was in use almost every day for six months, and was then in good condition. Fig. 2 shows diagrammatically the arrangement of the rheostats and the electric furnace.

The furnace employed to roast the argentiferous matte was

the American Gas Furnace Co.'s No. 4 Oven Furnace. It is shown in perspective in Fig. 3. The dimensions of the inner hearth were 18'' x 24''.

#### METHODS EMPLOYED.

The experiments were begun upon pure sulphates of the metals iron, copper, and silver, respectively. In order to determine at what temperatures these substances begin to decompose at atmospheric pressure by the agency of heat alone, each was taken separately and heated in the electric furnace until decomposition commenced. The thermo-electric couple of the pyrometer was placed in direct contact with the sulphate under treatment. The dissociation of the compound was attended with the absorption of heat. This absorption caused the arrest or retardation in the rate of change of temperature of the substance and couple, and the retardation was readily detected by the slower rate of movement of the galvanometer mirror of the pyrometer. The pyrometer having been previously calibrated,—*i.e.*, the relation of the amount of deflection of the galvanometer to the temperature of the thermo-couple having been ascertained,—the temperature at which the retardation occurred, which was the temperature at which the dissociation began, was thus easily recognized. As part of the sulphate was volatilized on dissociating, it was possible to confirm the results in each case gravimetrically. To confirm in this way, it was only necessary to take a fresh quantity of the sulphate and heat to a temperature just below the point indicated by the retardation, hold the temperature constant for some time, then cool and weigh. The balance, revealing no loss in weight, showed no change to have taken place. This was then heated a second time, this time to a temperature just above retardation, and maintained there for a few minutes. The loss in weight showed definitely that dissociation had taken place. In some cases analyses were made of the residues, to give further evidence of the decomposition.

In order to determine what were the products of the dissociation which began at a certain temperature, the substance was held at a temperature just a few degrees above that at which the reaction was seen to commence, until no further loss in weight was revealed. A constant temperature was maintained



in the furnace during this time, and the crucible and contents weighed at intervals. Many hours were often required for this condition of constant weight. The amount of loss indicated the products of the change, and analysis of the residue confirmed these indications.

It was found desirable to operate with small quantities in catching the exact temperature of retardation with the pyrometer. The couple could then be more conveniently placed in the layer of the sulphate next the crucible, in which layer the action of dissociation commenced. If the position of the point of contact of the couple in the sulphate was any appreciable distance from this first decomposing layer, the temperature of beginning dissociation came high; this effect being due to the influence of the atmosphere of sulphuric anhydride which surrounded the particles of the mass after the layer next the crucible began to decompose.

#### *Experiments with Copper Sulphate.*

A quantity of neutral copper sulphate or blue-vitriol crystals was dehydrated by heating to  $350^{\circ}$  C. and holding at that temperature for some time. The dehydrated salt was white, and remained so when kept in a stoppered bottle. A small amount of this dehydrated sulphate ( $\text{CuSO}_4$ ) was placed in a crucible with thin walls and inserted into the electric furnace. The magnesia crucible of the furnace was filled half full of powdered magnesium oxid, and the small porcelain crucible imbedded up to the rim in this powder (see Fig. 1), the idea being to get uniform heating around the sides of the crucible. The contact of the couple of the pyrometer was made as short as possible, in order that the uppermost point of the contact should be imbedded in the small amount of sulphate used. When the couple was in place, the heating-current of the furnace was turned on. Records of time and deflections of galvanometer were taken on blanks provided by the Metallurgical Department, as shown in Table II.

If the conditions of the experiment were carefully arranged, the retardation was decidedly marked, as is shown in the table. If for any cause the couple was not properly placed, the retardation came high, as already explained. As an average of a large number of such tests, the temperature of the first

TABLE II.—*Time of Deflection Readings for CuSO<sub>4</sub>.*

Series 3. Pieces Nos. 1 and 2. Date, March 6, 1902. Object, Dissociation of CuSO<sub>4</sub>. Reading by R. H. Bradford. Record by R. H. Bradford.

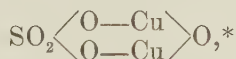
| Zero and Cold Junction. | Interval. | Time Rising. | Deflection. | Zero and Cold Junction. | Interval. | Time Rising. | Deflection. |
|-------------------------|-----------|--------------|-------------|-------------------------|-----------|--------------|-------------|
|                         | Sec.      | Min. Sec.    | Galv. Deg.  |                         | Sec.      | Min. Sec.    | Galv. Deg.  |
| .....                   |           |              | 6.0         | .....                   |           |              | 6.0         |
| .....                   |           |              | .1          | .....                   |           |              | .1          |
| .....                   |           |              | .2          | .....                   |           |              | .2          |
| .....                   |           |              | .3          | .....                   |           |              | .3          |
| .....                   |           |              | .4          | .....                   |           |              | .4          |
| 28° C.                  |           | 3-23         | .5          | 29° C.                  |           | 6-56         | .5          |
| .....                   | 22        | 45           | .6          | .....                   | 17        | 7-13         | .6          |
| .....                   | 22        | 3-07         | .7          | .....                   | 17        | 30           | .7          |
| .....                   | 23        | 30           | .8          | .....                   | 16        | 46           | .8          |
| .....                   | 24        | 54           | .9          | .....                   | 16        | 8-02         | .9          |
| .....                   | 28        | 5-22         | 7.0         | .....                   | 18        | 20           | 7.0         |
| .....                   | 35        | 57           | .1          | .....                   | 24        | 44           | .1          |
| .....                   | 37        | 6-34         | .2          | .....                   | 24        | 9-03         | .2          |
| .....                   | 38        | 7-12         | .3          | .....                   | 25        | 33           | .3          |

retardation for dehydrated copper sulphate (CuSO<sub>4</sub>) was found to be 653° C., and the inference was that this was the temperature at which sulphate of copper (CuSO<sub>4</sub>) begins to decompose by the application of heat alone.

In order to confirm this result, a weighed quantity (237 milligrammes) of the white dehydrated sulphate was placed in a small porcelain crucible, and the crucible and contents were introduced into the electric furnace and heated slowly to a temperature of 620° C. A constant temperature of 620° C. was maintained for five minutes; then the crucible and contents were removed, cooled and weighed. No loss of weight was observed, and the mass was still white. Again it was heated slowly, and the temperature of 645° C. maintained for a few minutes. No loss of weight, and no change of color to be seen. At the next heating the temperature of 650° to 655° C. was maintained for fifteen minutes, and on cooling a change in color from white to yellow was to be seen near the sides of the crucible, and a loss in weight of 13.1 per cent. of the original sulphate was revealed by the balance. Fumes of sulphuric anhydride were seen to rise out of the annular opening around the couple at the top of the cap of the furnace during the last heating. From these tests dissociation was seen to commence at a temperature between 650° and 655° C.; and the results confirmed those obtained by the retardation of the pyrometer.



To ascertain just how much of the sulphate would be volatilized at the temperature of  $653^{\circ}\text{C.}$ , and in this way to determine what the products of the dissociation were, 244 milligrammes of the white dehydrated sulphate were placed in a small platinum crucible and heated to  $655^{\circ}\text{C.}$  to  $670^{\circ}\text{C.}$  for two hours, and until no white salt remained and no further loss could be gotten. The substance had changed color from white to yellow. The loss in weight was 60.5 milligrammes, or 24.8 per cent. of the original weight. The experiment was repeated a number of times, and the average of the percentages of loss due to the dissociation, which began at  $653^{\circ}\text{C.}$ , was 25.04 per cent. The yellow salt did not change its color nor increase in weight from absorption of moisture from the atmosphere during four days that the substance was kept under observation. The yellow residues from two of these heatings were analyzed, and gave 53.5 per cent. and 53.12 per cent. copper respectively, with an average of 53.31 per cent. It was practically insoluble in distilled water, changing to a green color after a few minutes' time. From these tests the yellow residue was determined to be the basic copper sulphate of the formula  $\text{CuO},\text{CuSO}_4$ , or



in which the percentage of copper is 53.13 per cent. The theoretical loss in weight of two molecules of the neutral sulphate in changing to the basic salt is 25.07, as compared with 25.04 per cent. determined in these experiments. With the electric furnace it was possible to control the temperature so perfectly as to get all the white neutral salt changed to the yellow basic sulphate before any black oxid of copper was produced. This method of obtaining the yellow basic sulphate of copper from the white neutral sulphate had been previously attempted, but without success.† This may be accounted for by the facts that the dissociation proceeds very slowly when the temperature is raised but a few degrees above the point at which the change begins; and that, at a temperature less than  $50^{\circ}$  higher, the yellow basic salt begins to dissociate with the formation of black oxid of copper and sulphuric anhydride.

\* Roscoe & Sch., vol. ii., pt. i., p. 339.

† S. U. Pickering, *Chemical News*, vol. xlvii., p. 182.

The speed of dissociation was much slower when the furnace was kept closed, so that the atmosphere within the crucible was one of sulphuric anhydride, than when the furnace was open at the top, allowing the ingress of air. Even with an open furnace, considerable time was required for the action to become complete. If the material was heated rapidly, it was possible to raise the temperature many degrees above the point at which the decomposition commenced without effecting a complete change. If the gaseous products of the dissociation were rapidly removed, the effect was to greatly hasten the operation. In roasting the argentiferous copper mattes—especially was this noticed in the muffle-furnace—the speed of dissociation was greatly increased by providing for the rapid removal of the gaseous products.

*Treatment of the Yellow Basic Sulphate.*

Experiments were carried out with the yellow basic sulphate, obtained by decomposing the white neutral salt, in a manner similar to that already described for the dehydrated blue vitriol. Small quantities were taken in a porcelain crucible and heated in the electric furnace with a uniformly rising temperature. The point of contact of the thermo-couple was imbedded in the yellow powder next the crucible. The time-deflection readings are illustrated in Table III.

TABLE III.—*Time-Deflection Readings for  $\text{CuO}, \text{CuSO}_4$ .*

Series 4. Nos. 3 and 4. Date, March 8, 1902. Object,  $\text{CuO}, \text{CuSO}_4$  to  $\text{CuO}$ . Reading by R. H. B. Record by R. H. B.

| Zero and Cold Junction. | Interval | Time Rising. | Deflection. | Zero and Cold Junction. | Interval. | Time Rising. | Deflection. |
|-------------------------|----------|--------------|-------------|-------------------------|-----------|--------------|-------------|
|                         | Sec.     | Min. Sec.    | Galy. Deg.  |                         | Sec.      | Min. Sec.    | Galy. Deg.  |
| 29° C.                  | .....    | 2-55         | 7.0         | 27° C.                  | .....     | 4-26         | 7.0         |
| .....                   | 31       | 3-26         | .1          | .....                   | 20        | 46           | .1          |
| .....                   | 31       | 57           | .2          | .....                   | 21        | 5-07         | .2          |
| .....                   | 32       | 4-29         | .3          | .....                   | 20        | 27           | .3          |
| .....                   | 33       | 5-02         | .4          | .....                   | 21        | 48           | .4          |
| .....                   | 32       | 34           | .5          | .....                   | 24        | 6-12         | .5          |
| .....                   | 33       | 6-07         | .6          | .....                   | 28        | 40           | .6          |
| .....                   | 39       | 46           | .7          | .....                   | 29        | 7-09         | .7          |
| .....                   | 41       | 7-27         | .8          | .....                   | 31        | 40           | .8          |
| .....                   | 40       | 8-07         | .9          | .....                   | 32        | 8-12         | .9          |
| .....                   | 40       | 47           | 8.0         | .....                   | 31        | 43           | 8.0         |
| .....                   | 40       | 9-27         | .1          | .....                   | .....     | .....        | .1          |



Six different trials with the basic sulphate gave the temperatures of retardation as follows:  $700^{\circ}$  C.,  $703^{\circ}$  C.,  $701^{\circ}$  C.,  $705^{\circ}$  C.,  $700^{\circ}$  C. and  $703^{\circ}$  C., giving an average of the six as  $702^{\circ}$  C.

To confirm these results, a weighed quantity of the yellow salt was heated for ten minutes at a temperature of  $690^{\circ}$ – $695^{\circ}$  C., then cooled and weighed. No change of weight had occurred, and the color remained the same. This was heated again—this time to  $705^{\circ}$ —for 10 minutes. On cooling, a layer of black oxid was to be seen next to the crucible, and a loss in weight showed that the temperature of dissociation had been reached. A number of continued heatings at temperatures of  $705^{\circ}$ – $720^{\circ}$  C. showed that it was only necessary to allow sufficient time to effect complete change to the black oxid, as was indicated by the loss in weight and change in color, and confirmed by analyses of the residues. Time was found to be an important factor in effecting the complete dissociation; but, as would be expected, the time required was less, the greater the temperature of beginning dissociation was exceeded. With but one gramme of the basic sulphate in the crucible, the mass could be raised to  $750^{\circ}$  C., and still have the change to oxid incomplete. With 4 or 5 grammes of the substance, the temperature could be brought to  $850^{\circ}$  C. and higher, without complete change taking place. If the neutral sulphate were heated more or less rapidly, the dissociation into basic salt began at  $653^{\circ}$  C.; but while this change was taking place, the atmosphere of sulphuric anhydride evolved retarded the change of the basic sulphate to the oxid, so that a temperature above  $702^{\circ}$  C. could be obtained without the appearance of any black oxid.

From these experiments on blue vitriol ( $\text{CuSO}_4 + \text{Aq}$ ), it is seen that the neutral sulphate commences to change to the basic sulphate at the temperature of  $653^{\circ}$  C., and that cupric oxid begins to form at a temperature of  $702^{\circ}$  C. If these temperatures be not exceeded but slightly, and if the sulphuric anhydride is not readily removed, the change is slow. A higher temperature and a more open furnace effects a more rapid action.

*Experiments with Ferrous Sulphate.*

A crystal of chemically pure green vitriol ( $\text{FeSO}_4 + 7\text{Aq}$ ), weighing 840 milligrammes, was heated in a small porcelain

crucible arranged in the furnace in the same manner as described for copper sulphate. After dehydrating, the mass was pressed down onto the bottom of the crucible, and the junction of the thermo-electric couple was imbedded in the powder. The heating-current of the furnace was turned on, and the temperature rose slowly, though not so uniformly as in the case of the sulphates of copper. As a temperature of  $585^{\circ}$  C. was reached, a retardation in the rate of heating was indicated, as shown in Table IV.

TABLE IV.—*Time-Deflection Readings for  $FeSO_4$ .*

| Zero and Cold Junction. | Interval. | Time Rising. | Deflection. | Zero and Cold Junction. | Interval. | Time Rising. | Deflection. |
|-------------------------|-----------|--------------|-------------|-------------------------|-----------|--------------|-------------|
|                         | Sec.      | Min. Sec.    | Galv. Deg.  |                         | Sec.      | Min. Sec.    | Galv. Deg.  |
| .....                   |           |              | 5.1         | .....                   |           |              | 5.1         |
| .....                   |           |              | .2          | .....                   |           |              | .2          |
| .....                   |           |              | .3          | .....                   |           |              | .3          |
| .....                   |           |              | .4          | .....                   |           |              | .4          |
| .....                   |           | 5-43         | .5          | .....                   |           | 6-40         | .5          |
| .....                   | 11        | 54           | .6          | .....                   | 11        | 51           | .6          |
| .....                   | 11        | 6-05         | .7          | .....                   | 12        | 7-03         | .7          |
| .....                   | 11        | 16           | .8          | .....                   | 14        | 17           | .8          |
| .....                   | 12        | 28           | .9          | .....                   | 15        | 32           | .9          |
| .....                   | 11        | 39           | 6.0         | .....                   | 15        | 47           | 6.0         |
| 28° C.                  | 13        | 52           | .1          | .....                   | 15        | 8-02         | .1          |
| .....                   | 12        | 7-04         | .2          | 27° C.                  | 15        | 17           | .2          |
| .....                   | 15        | 19           | .3          | .....                   | 17        | 34           | .3          |
| .....                   | 16        | 35           | .4          | .....                   | 19        | 53           | .4          |
| .....                   | 16        | 51           | .5          | .....                   | 20        | 9-13         | .5          |
| .....                   | 17        | 8-08         | .6          | .....                   | 20        | 33           | .6          |

The retardation is seen to be slight; yet, from a number of concordant results, the retardation was observed to occur regularly at the same temperature of  $590^{\circ}$  C.

Attempts to confirm this result by heating weighed quantities of the ferrous salt in an open crucible and noting the temperature at which loss in weight was first observed were not successful, owing to the fact that the ferrous sulphate tends to oxidize when heated in the presence of air. It was found that, after dehydrating, if the substance were heated to successive temperatures above  $300^{\circ}$  C., and held for half an hour, an increase in weight was observed in every case, until a temperature of about  $535^{\circ}$  C. was reached. Above this temperature a reduction in weight was revealed. The amount of increase in weight for half an hour at  $515^{\circ}$  C. was only 1.03 per cent. A

portion heated to  $535^{\circ}$  for twelve minutes showed absolutely no change in weight, and, when heated to  $540^{\circ}$  C. for two and a half hours, gave a decrease of 5 per cent. of the original ferrous salt employed. The rate of decrease was slightly greater at  $550^{\circ}$  C., and at  $565^{\circ}$  still greater. The tendency of the ferrous salt to become oxidized in air accounts for the increase in weight referred to. The reduction in weight which began below  $590^{\circ}$  C. was undoubtedly due to the fact that the ferric sulphates formed by the partial oxidation of the ferrous sulphate dissociate at a lower temperature than does the ferrous salt itself.

To overcome the difficulty of oxidation which takes place in an open vessel, a sample of the ferrous sulphate was heated in a glass bulb-tube, three inches long, and drawn out at a point near the substance to an internal diameter of  $\frac{1}{8}$  of an inch. The bulb containing the substance was placed in the powder within the magnesia crucible of the furnace, and the other end of the tube extended up through the cap of the furnace. In this tube the oxidation was inappreciable. The weight remained constant, as shown by the balance after each successive heating of 10 to 20 minutes to temperatures between  $500^{\circ}$  and  $585^{\circ}$  C. When a temperature of  $590^{\circ}$  C. was reached, fumes of  $\text{SO}_3$  appeared at the mouth of the tube. The tube was kept at  $590^{\circ}$  C. for 30 minutes, and then cooled and weighed, and a loss of weight showed the dissociation to have commenced. The loss was very slight, but a sublimate of sulphuric anhydride, which rapidly charred to sulphuric acid, was observed near the cooler end of the tube. The dissociation was extremely slow in this tube, as instanced by the fact that when the temperature was held at  $625^{\circ}$ – $635^{\circ}$  C. for 2 hours, a loss of weight of only 3 per cent. was effected. This showed the decided effect on the rate of dissociation of a dense atmosphere of the sulphuric anhydride evolved.

#### *Silver Sulphate.*

Silver sulphate was prepared by dissolving pure metallic silver in boiling sulphuric acid and evaporating to dryness or until every trace of free acid was removed. A porcelain evaporating dish was used, and care was taken not to allow the gas flame of the Bunsen burner to play over the dish. In the presence of reducing-gases, the sulphate of silver was decomposed



at a very moderate heat, metallic silver being deposited. Three grammes of the silver sulphate thus prepared were placed in a Royal Meissen porcelain crucible and heated in the electric furnace. The junction of the couple of the pyrometer was placed in direct contact with the salt for investigations up to a temperature near  $850^{\circ}\text{C}$ . For higher temperatures the couple was enclosed in a porcelain tube of  $\frac{3}{8}$ -in. internal diameter, 4 in. long, closed at lower end. The temperature rose uniformly until  $660^{\circ}\text{C}$ . was reached, when the substance melted, causing a decided arrest or retardation of the pyrometer. On cooling, the freezing-point of the sulphate was readily indicated in a similar way. The freezing-point came at  $655^{\circ}\text{C}$ .,\* a few degrees below the melting-point in every case. No further irregularity in the rate of heating and no disturbance in the liquid sulphate could be observed until a temperature of  $1095^{\circ}\text{C}$ . was attained. Here the liquid filled with bubbles, and quantities of sulphuric anhydride were evolved. If the temperature were held at  $1095^{\circ}\text{C}$ ., the evolution of gas proceeded rapidly until all was decomposed, leaving molten metallic silver in the crucible. But if the furnace was allowed to cool a few degrees, the reaction ceased, and the liquid sulphate again became quiescent. The experiment was repeated a number of times, and the rapid evolution of gas commenced in each case at  $1095^{\circ}\text{C}$ .

In the next experiments, to determine if any decomposition occurred when the sulphate was heated to, and maintained at, temperatures below that of this rapid dissociation, 1.195 grammes of the sulphate were heated to  $866^{\circ}\text{C}$ . for five minutes. No metallic silver appeared, and the balance indicated no appreciable loss in weight. On heating to  $970^{\circ}\text{C}$ . for five minutes, the loss in weight amounted to 3.5 milligrammes, or  $\frac{1}{3}$  of 1 per cent. Again the mass was heated, this time to  $1050^{\circ}\text{C}$ ., for five minutes. The loss was 25 milligrammes, or over 2 per cent., and metallic silver appeared in globules around the crucible. A fresh quantity of the salt weighing 2.966 g. was heated for one hour and twenty minutes to a temperature of  $900^{\circ}\text{C}$ . On cooling, particles of metallic silver adhered to the sides of the vessel. The analytical balance showed a loss of weight of 46 milligrammes, or 1.6 per

\* Carnelly gives the freezing-point of the sulphate of silver as  $654 \pm 2$ . *Journal of the Chemical Society*, vol. xxix., p. 489.

cent. On heating the same mass to  $920^{\circ}$  C. for an hour and thirty minutes, a thin layer of metallic silver covered the unchanged sulphate, which layer became somewhat thicker after heating to  $945^{\circ}$  C. for one hour. The loss in weight had now reached 6 per cent., showing one-fifth of the sulphate to be decomposed.

In order to determine whether the reduction of metallic silver at temperatures as low as  $900^{\circ}$  C. was not due to the reaction of the sulphate on the porcelain of the crucible, these experiments were repeated in a platinum vessel. The results with the platinum vessel confirmed those with the porcelain crucible, and are given in Table V., along with those with the porcelain crucible.

TABLE V.—*Rate of Dissociation of  $Ag_2SO_4$  at Different Temperatures.*

| Quantity of $Ag_2SO_4$ . | Kind of Crucible. | Temp. to which Substance was Heated. | Time during which the Temperature Remained Constant. | Loss in Weight. | Percentage Loss. | Remarks.            |
|--------------------------|-------------------|--------------------------------------|------------------------------------------------------|-----------------|------------------|---------------------|
|                          |                   | C.                                   |                                                      | gr.             | Per Cent.        |                     |
| 1.800 g.                 | Platinum.         | $750^{\circ}$                        | 10 min.                                              | No loss         | .....            | .....               |
| "                        | "                 | $825^{\circ}$                        | 10 "                                                 | 0.002           | 0.11             | No silver.          |
| "                        | "                 | $850^{\circ}$ – $860^{\circ}$        | 15 "                                                 | 0.004           | 0.22             | "                   |
| "                        | "                 | $850^{\circ}$                        | 40 "                                                 | 0.004           | 0.22             | "                   |
| "                        | "                 | $880^{\circ}$ – $890^{\circ}$        | 3 hours.                                             | 0.180           | 10.00            | Much silver.        |
| 1.195 g.                 | Porcelain.        | $866^{\circ}$                        | 5 min.                                               | trace.          | .....            | .....               |
| "                        | "                 | $970^{\circ}$                        | 5 "                                                  | 0.0035          | 0.30             | .....               |
| "                        | "                 | $1050^{\circ}$                       | 5 "                                                  | 0.025           | 2.10             | .....               |
| 2.963 g.                 | "                 | $900^{\circ}$                        | 1 hr. 20 min.                                        | 0.046           | 1.60             | Globules of silver. |
| 1.302 g.                 | "                 | $900^{\circ}$                        | 40 min.                                              | 0.008           | 0.62             | .....               |
| 0.619 g.                 | "                 | $880^{\circ}$ – $920^{\circ}$        | 15 "                                                 | 0.009           | 1.45             | .....               |
| "                        | "                 | $1020^{\circ}$                       | .....                                                | 0.0155          | 2.50             | .....               |
| 0.8515 g.                | "                 | $955^{\circ}$                        | 30 min.                                              | 0.005           | 0.6              | .....               |
| "                        | "                 | $965^{\circ}$                        | 30 "                                                 | 0.009           | 1.05             | .....               |
| 0.743 g.                 | "                 | $1010^{\circ}$                       | 1 hr. 20 min.                                        | 0.053           | 7.10             | Globules of silver. |

After maintaining the silver sulphate in the platinum vessel at temperatures of  $825^{\circ}$  C.,  $860^{\circ}$  C. and  $850^{\circ}$  C., respectively, for periods of time amounting in all to one hour and five minutes, the total loss in weight was less than 0.6 per cent., and no metallic silver could be found. After fifteen minutes at  $900^{\circ}$  C. the loss amounted to more than double that which had occurred during the whole hour at the lower temperatures, and metallic silver was to be seen around the vessel. After three hours at  $880^{\circ}$ – $890^{\circ}$  C. the loss had reached nearly 12 per cent.,

showing 40 per cent. of the sulphate to be decomposed. The loss in weight by continuous heating could be detected at any temperature above its melting-point ( $655^{\circ}$  C.). Below  $860^{\circ}$ – $870^{\circ}$  C. this loss was extremely small, and no metallic silver appeared even after an hour's time, so that the loss seemed to be due to the evaporation of the molten sulphate as such rather than to the dissociation of the salt. At temperatures of  $860^{\circ}$ – $870^{\circ}$  C., and above, the loss in weight was much more rapid, and the deposition of metallic silver indicated the decomposition of the silver sulphate. But not until  $1095^{\circ}$  C. was reached was there any agitation of the liquid due to the formation of bubbles of gas throughout the substance.

In roasting argentiferous copper mattes the silver sulphate formed is associated with the oxids of iron and copper. To determine whether these oxids have any effect on the dissociation of the sulphate of silver, the sulphate was heated with many times its weight of (1) cupric oxid, and (2) silica, and (3) ferric oxid. The reduction of metallic silver was found to be much more rapid when either of these oxids was present, as shown in Tables VI., VII. and VIII. In each case the reduction commenced at the same temperature, and this temperature corresponded with that at which the dissociation began when the sulphate was heated alone, viz.,  $860^{\circ}$ – $870^{\circ}$  C. When heated to  $870^{\circ}$ – $890^{\circ}$  C. for three hours with four times its weight of cupric oxid, the sulphate was all reduced; while the sulphate alone, for an equal time, at the same temperature, showed a loss of only 10 per cent., corresponding to a decomposition of but  $\frac{1}{3}$  of the sulphate present. When heated with either silica or ferric oxid, the decomposition above  $860^{\circ}$ – $870^{\circ}$  C. was fully as rapid as with cupric oxid. (See Tables VII. and VIII.).

TABLE VI.—*Results of Heating Sulphate of Silver and CuO.*

| Quantity of Substances.                                         | Kind of Crucible. | Temp. to which Substance was Heated. | Time during which the Temp. Remained Constant. | Loss in Weight. | Percentage Loss.             | Remarks.    |
|-----------------------------------------------------------------|-------------------|--------------------------------------|------------------------------------------------|-----------------|------------------------------|-------------|
| gr.<br>{ $\text{Ag}_2\text{SO}_4$ 0.3235<br>$\text{CuO}$ 0.8155 | Porcelain.        | Deg. C.<br>820                       | 5 min.                                         | gr.<br>0.0015   | .....                        | .....       |
| “                                                               | “                 | 875                                  | 5 “                                            | 0.009           | .....                        | .....       |
| “                                                               | “                 | 875                                  | 15 “                                           | 0.018           | .....                        | .....       |
| “                                                               | “                 | 870                                  | 55 “                                           | 0.0525          | .....                        | .....       |
| “                                                               | “                 | 880                                  | 1 hr. 20 m.                                    | 0.019           | All $\text{Ag}_2\text{SO}_4$ | Decomposed. |



TABLE VII.—*Sulphate of Silver and Silica.*

| Quantity of Substances.                                          | Kind of Crucible. | Temp. to which Substance was Heated. | Time during which the Temp. Remained Constant. | Loss in Weight. | Remarks.              |
|------------------------------------------------------------------|-------------------|--------------------------------------|------------------------------------------------|-----------------|-----------------------|
| gr.<br>{ $\text{Ag}_2\text{SO}_4$ 0.471<br>$\text{SiO}_2$ 0.3475 | Porcelain.        | Deg. C.<br>770                       | 30 min.                                        | gr.<br>None.    | .....                 |
| “                                                                | “                 | 815                                  | 5 “                                            | None.           | .....                 |
| “                                                                | “                 | 810                                  | 5 “                                            | None.           | .....                 |
| “                                                                | “                 | 860                                  | 5 “                                            | None.           | .....                 |
| “                                                                | “                 | 870                                  | 2 “                                            | 0.011           | Much metallic silver. |
| “                                                                | “                 | 870–900                              | 30 “                                           | 0.051           | Much metallic silver. |

TABLE VIII.—*Sulphate of Silver and Ferric Oxid.*

| Quantity of Substances.                                                  | Kind of Crucible. | Temp. to which Substance was Heated. | Time during which the Temp. Remained Constant. | Loss in Weight. | Remarks.              |
|--------------------------------------------------------------------------|-------------------|--------------------------------------|------------------------------------------------|-----------------|-----------------------|
| gr.<br>{ $\text{Ag}_2\text{SO}_4$ 0.535<br>$\text{Fe}_2\text{O}_3$ 0.630 | Porcelain.        | Deg. C.<br>850                       | 10 min.                                        | gr.<br>0.001    | No silver.            |
| “                                                                        | “                 | 870–890                              | 10 min.                                        | 0.0053          | Some metallic silver. |
| “                                                                        | “                 | “                                    | 1 hr. 30 m.                                    | 0.080           | Much silver.          |

If cuprous oxid ( $\text{Cu}_2\text{O}$ ) is added to a solution of silver sulphate in water, metallic silver is reduced and appears as spangles according to the following equation:  $\text{Ag}_2\text{SO}_4 + \text{Cu}_2\text{O} = \text{CuO} + \text{CuSO}_4 + 2\text{Ag}^*$  (called the spangle reaction). Since silver sulphate is in the molten condition above  $655^\circ \text{C}$ ., it was thought that the presence of cuprous oxid in the roast might cause a reduction of silver from the molten sulphate. It was impossible to ascertain by the loss of weight method just when the sulphate of silver began to decompose on being heated with cuprous oxid, as some of the lower oxid of copper became oxidized to the higher oxid by the oxygen of the atmosphere, with a corresponding increase in weight. This increase could have more than offset the loss due to the reduction of the sulphate of silver. It was therefore necessary to adopt some other method of ascertaining just when this change commenced, providing it did occur. After each heating, some of the mixture was removed from the crucible and examined with a microscope for particles of metal.

\* Balling, *Metallurgische Chemie*, p. 58. Plattner, “Grillage.”

lic silver. No indication of the metal could be found until the temperature rose to the point at which the change began with the sulphate alone, or with the sulphate in the presence of the other oxids, viz., 860°–870° C. Tabulated results of these heatings are given in Table IX.

TABLE IX.—*Sulphate of Silver with Cuprous Oxids.*

| Quantity of Substances.          | Kind of Crucible. | Temp. to which Substance was Heated. | Time during which the Temp. Remained Constant. | Increase in Weight. | Remarks.                |
|----------------------------------|-------------------|--------------------------------------|------------------------------------------------|---------------------|-------------------------|
| gr.                              |                   | Deg. C.                              |                                                | gr.                 |                         |
| { $\text{Ag}_2\text{SO}_4$ 0.215 | Porcelain.        | 670                                  | 5 min.                                         | 0.088               | .....                   |
| { $\text{Cu}_2\text{O}$ 1.028    | "                 | 805                                  | 5 "                                            | 0.008               | .....                   |
| "                                | "                 | 825                                  | 5 "                                            | 0.007               | .....                   |
| "                                | "                 | 861                                  | 5 "                                            | 0.003               | No metallic silver.     |
| "                                | "                 | 900                                  | 30 "                                           | Loss                |                         |
| "                                | "                 | 900                                  | 10 "                                           | 0.004               | Metallic silver appears |
|                                  |                   |                                      |                                                | 0.015               | Much metallic silver.   |

### *Cuprous Oxid.*

Cuprous oxid reduces metallic silver from a solution of silver sulphate. This reaction is readily obtained by adding cuprous oxid to a solution of the sulphate of silver in a test-tube. The silver is reduced, and, upon shaking, spangles of the metal float about in the liquid. Owing to this reaction there must be no cuprous oxid in the roasted matte when ready for leaching. During the earlier stages of the roast, while considerable sulphur in the sulphide condition is present, more or less of the cupric oxid is reduced to the cuprous state through the reducing action of these sulphides. This lower oxid must be reoxidized by continuing the roasting operation with excess of air before leaching is begun. It is also known that cupric oxid is reduced to cuprous oxid by heat alone\* at a high temperature. To determine at what temperature this reduction to cuprous oxid occurs, a series of experiments were carried out.

A quantity of crystallized copper sulphate was dehydrated, and then heated to a temperature of 840° C. until the whole was decomposed to black oxid, as indicated by its color and by the loss in weight. A weighed portion of this cupric oxid was

\* Favre a. Maumene, *Comptes Rendus*, 18, 658. Debray and Joannis, *Comptes Rendus*, 99, 383.

heated in a porcelain crucible in the electric furnace. The couple of the pyrometer was placed in direct contact with the black powder. The heating current of 36 amperes was turned on, and the temperature rose rapidly. Readings of time and deflections of the galvanometer were recorded after the temperature rose above  $840^{\circ}\text{C}$ . The mirror of the galvanometer moved regularly up to  $1050^{\circ}\text{C}$ ., where a slight retardation was detected. The change in rate of movement of the galvanometer mirror was very slight, but repeated experiments seemed to indicate some change at this temperature. To determine whether this was the temperature at which dissociation of cupric oxid into cuprous oxid and oxygen commenced, the gravimetric method was employed. Three hundred and thirty-eight milligrammes of cupric oxid were heated to  $900^{\circ}\text{C}$ ., then cooled and weighed. The analytical balance revealed no loss in weight. Again to  $945^{\circ}\text{C}$ .,  $1000^{\circ}\text{C}$ . and  $1045^{\circ}\text{C}$ . respectively, with the same results. The heated oxid was cooled slowly in the furnace in some instances, and in others rapidly in open air. No loss in weight could be obtained up to  $1045^{\circ}\text{C}$ . After heating to a temperature slightly above  $1050^{\circ}\text{C}$ ., the highest point being  $1065^{\circ}\text{C}$ ., a loss in weight of  $1\frac{1}{2}$  per cent. indicated a partial change to have taken place. The loss was increased to 4.5 per cent. by heating again to the same temperature for ten minutes. The Royal Meissen crucible gave most uniform results. With some other makes of crucible the oxid of copper seemed to react with the crucible at temperatures below  $1050^{\circ}\text{C}$ ., occasioning at times a loss in weight. The experiments were repeated a number of times with a platinum dish in place of the porcelain one. Some results with the platinum dish are as follows: 611 milligrammes of cupric oxid were heated to  $1000^{\circ}\text{C}$ . for fifty minutes, and cooled rapidly out of the furnace. No change in color nor loss in weight. Again to  $1035^{\circ}\text{C}$ – $1045^{\circ}\text{C}$ . for three hours, with like results. No change could be effected up to  $1045^{\circ}\text{C}$ . After heating again to  $1050^{\circ}\text{C}$ – $1060^{\circ}\text{C}$ ., a loss in weight indicated a partial reduction to the lower oxid.

*Fusion of the Reduced Oxid.*—The reduction was found to proceed slowly at temperatures but slightly above that at which it began. If the temperature were raised much above  $1050^{\circ}\text{C}$ . not only a reduction but fusion occurred. When the sub-



stance was heated rapidly, so that time was not given for reduction to become complete, a temperature as high as  $1150^{\circ}\text{C.}$  was obtained without fusion. If time were allowed for complete reduction to take place but slightly above  $1050^{\circ}\text{C.}$ , the reduced mass fused at a temperature of  $1065^{\circ}\text{C.}$  This fused oxid solidified at a temperature near  $1050^{\circ}$ , the temperature at which reduction begins. This melting-point and freezing-point of the reduced oxide were found to remain constant, as revealed by the retardation of the pyrometer; but if time were not given for complete reduction to be effected before fusion occurred, a mixture of the cupric and cuprous oxids, with a higher melting-point, would result.

In every case, after this reduction to the lower oxid, the upper portion of the mass was again oxidized to cupric oxid when cooled in air. From this action the question was suggested: Did the reduction begin at a lower temperature than that indicated by the above experiments, and escape detection by the balance because of reoxidation? Fresh portions of the higher oxid were heated to and held at temperatures ranging from  $800^{\circ}\text{C.}$  to  $1100^{\circ}\text{C.}$ , and cooled in an atmosphere of nitrogen.

*Methods of Preparing and Using Nitrogen.*

The nitrogen gas was prepared by passing air through heated ammonia-water and then over heated shot-copper contained in a glass combustion-tube. This tube was two feet long, and was kept red hot by an ordinary combustion-furnace. From the tube the gas was conducted through two wash-bottles, one containing sulphuric acid and the other an alkaline solution of pyrogalllic acid, and then into a gas-tank. After the copper in the tube was heated to redness, the apparatus was connected up and the current of air and ammonia passed through. The necessary suction was produced to draw the gases through the apparatus by operating a siphon from the inner side tube of the gas-tank. Oxidation began at the inlet end of the tube, and a portion of the copper-shot was coated with red oxid. The oxid of copper reacted on the ammonia, extracting its hydrogen and setting nitrogen free, the cuprous oxid being reduced by the reaction to metallic copper.



This reducing action of the ammonia gave fresh surfaces of metallic copper for extracting the oxygen from the current of air. The excess of ammonia and the water formed in the process were collected by the sulphuric acid in the first wash-bottle. The alkaline solution of pyrogallie acid was provided to take up any oxygen which the metallic copper did not extract. The nitrogen collected came partly from the air and partly from the ammonia.

It was found to be necessary to operate slowly, in order that the reaction in the tube should be complete. As a further precaution, the tank of nitrogen collected was again passed through the tube of heated copper and through fresh solutions, to make sure that every trace of oxygen was removed. No trace of either oxygen or ammonia could be detected in the nitrogen from this second tank.

All the openings and joints of the electric furnace were luted with fire-clay except the annular space around the porcelain tube which carried the couple through the cap, after the crucible with the cupric oxid had been placed in position. The oxid was heated to the desired temperature and held there for some minutes; then the porcelain tube and couple were removed, and a similar tube, open at both ends, was placed in the opening through the cap, the lower end of the tube coming next to the heated oxid. This tube was connected with the gas-tank—nitrogen had been passed through the rubber tubing and porcelain tube to remove the air from them—and the nitrogen was turned on. The heating-current was cut off and the furnace and contents allowed to cool. In this way the cooling oxid was continuously surrounded by an atmosphere of nitrogen.

A brief description of these tests, and the results of the same, are here given: 1.735 grammes of cupric oxid were heated to  $950^{\circ}$  C. for fifteen minutes, then cooled in an atmosphere of nitrogen as above described. The analytical balance revealed no loss in weight, and the color remained black. No change had occurred at this temperature. Another sample was heated to  $1035^{\circ}$  C. for ten minutes, and cooled in nitrogen. No change in color and no loss in weight could be detected. On heating the same again to  $1065^{\circ}$  for ten minutes, and cooling in a similar manner, the color had changed to reddish brown,

and the balance revealed a loss in weight of 8 per cent. After heating for twenty minutes to the same temperature, and cooling in nitrogen again, the loss was found to be increased to 9 per cent., out of a possible 10 per cent., which is the calculated loss for a complete change of cupric into cuprous oxid.\*

These results confirmed those without the nitrogen, except that the reductions as shown by the balance for temperatures above  $1050^{\circ}\text{C.}$ , were greater for corresponding lengths of time. This was due to the absence of reoxidation in the atmosphere of nitrogen. No reduction to the lower oxid was found for temperatures below  $1050^{\circ}\text{C.}$

The dissociation of the higher oxid of copper into the lower oxid was found by the above-described experiments to occur at  $1050^{\circ}\text{C.}$ , a temperature nearly 50 degrees below that at which the rapid reduction of silver sulphate begins, but nearly 200 degrees above that temperature at which silver sulphate commences to decompose slowly when alone, and more rapidly in the presence of the oxids of copper and iron. This reduction of cupric to cuprous oxid by heat alone is, therefore, not of importance in the Ziervogel process, as it is effected only at a temperature two hundred degrees above that at which the roasting mass can safely be heated, because of other reactions.

### *Magnetic Oxid of Iron.*

Magnetic oxid of iron reduces metallic silver from a solution of silver sulphate† according to the following equation:  $4\text{Fe}_3\text{O}_4 + \text{Ag}_2\text{SO}_4 = 6\text{Fe}_2\text{O}_3 + \text{SO}_2 + 2\text{Ag}$ . This reaction is much less rapid than that of the reduction of the metal by cuprous oxid. The reaction is so slow that the presence of small quantities of the magnetic oxid in the roasted matte is not fatal to the leaching process, as is shown by the following experiment: 50 milligrammes of silver sulphate were placed in each of two small beakers and dissolved in hot water. To one was added one gramme of finely powdered magnetic oxid of iron. The oxid employed was magnetite from Port Henry, N. Y. The solution, with the powdered magnetite, was heated for ten minutes near the boiling-point of water. This solution was

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\*  $2\text{CuO} = \text{Cu}_2\text{O} + \text{O}$   
(160) = (144) (16)

† Plattner *Grillage*, p. 141, par. 3. Balling, "*Metallurgische Chemie*," p. 57.



then filtered and washed, and both the solutions of sulphate were titrated with ammonium-sulpho-cyanate. The results of the titration showed 7.6 c.c. for the solution which had been treated with the magnetic oxid, and 7.8 c.c. for the other solution. The loss due to the magnetic oxid was only 2.56 per cent.

When ferric oxid ( $\text{Fe}_2\text{O}_3$ ) is subjected to a high temperature it is reduced to magnetic oxid ( $\text{Fe}_3\text{O}_4$ ). To determine at what temperature this reduction occurred, providing it came within the limits of temperature allowable in the Ziervogel process, a series of experiments were carried out in a manner similar to those described for cupric oxid. It was found that no reduction to magnetic oxid was effected until a temperature above  $1100^\circ \text{C.}$  was reached. The exact temperature at which dissociation commenced was not definitely determined. The tests, however, showed that the change of ferric to magnetic oxid by heat alone, coming at so high a temperature, was not of importance in the roasting process.

#### *Oxidation of the Sulphides.*

The temperature at which the sulphide begins to oxidize in a current of air was not determined for each individual sulphide. It was found on roasting copper mattes in the oven-furnace that, owing to the large amount of sulphur in them, as soon as rapid oxidation commenced, the temperature rose rapidly to  $450^\circ$  to  $500^\circ \text{C.}$  Since an excess of air is desirable to get the oxidation to the sulphate\* instead of the formation of  $\text{SO}_2$  and the oxids of copper, this rapid rise in temperature cannot be readily prevented. The principal part of the oxidations occurs above  $450^\circ \text{C.}^\dagger$  The exact temperature at which oxidation commences is of little consequence in the process.

#### ROASTING OF ARGENTIFEROUS COPPER MATTES.

The operation of roasting the argentiferous mattes was carried on in the gas oven-furnace described and illustrated in Fig. 3. Temperatures up to  $900^\circ \text{C.}$  could be readily obtained in the furnace, and by regulating the gas and blast, the heat

\* "The Metallurgy of Argentiferous Compounds." H. M. Howe. *Production of Gold and Silver in the U. S.*, Burchard, Washington, 1883, p. 757.

† Steinbeck, *Chem.-Analy. Untersuchungen*, p. 49.

was easily kept under control. Cast-iron trays were employed to receive the matte, and these were placed directly upon the fire-brick hearth. The trays were 20 in. long and 5 in. wide by  $\frac{3}{4}$ -in. deep, inside dimensions; and the sides and bottom were of uniform thickness of  $\frac{3}{8}$ -in. Rakes and rabblers of such size as could be worked through the two port-holes in the furnace-door were used to stir the roasting charge. An iron spoon attached to the end of a  $\frac{3}{8}$ " rod, and small enough to be inserted into the port-holes, served for taking samples at the various stages of the roast.

The platinum and platinum-rhodium wires of the pyrometer were strung through a doubly-perforated fire-clay tube,  $\frac{3}{8}$ -in. external diameter. At the end of this long tube, next the junction of the wires, was arranged a short length of doubly-perforated tube of somewhat smaller diameter. By means of this short length, the junction of the couple could be readily raised and lowered, in the material whose temperature was sought, without disturbing the longer tube. When the furnace-door was open, the tubes were passed into the furnace through the open door. If it was necessary to close the door, the tubes were run in through one of the port-holes. The water-bottle containing the cold junctions of the pyrometer was placed on a stand near the furnace-door. The thermo-electric couple was kept within the furnace during the entire time the matte was roasting.

A number of mattes with varying amounts of iron, copper, and silver, were treated, and the samples taken at the different stages of the process analyzed. The matte with which most of the experimental work was done had the composition given in Table X. It was obtained from the Orford Copper Works at Bergen Point, N. J., and its silver content enriched to 100 oz. per ton.

TABLE X.—*Composition of the Argentiferous Matte.*

|                     | Per cent.             |
|---------------------|-----------------------|
| Copper, . . . . .   | 50.80                 |
| Iron, . . . . .     | 22.64                 |
| Sulphur, . . . . .  | 25.80                 |
| Silver, . . . . .   | 0.31 (100 oz. to ton) |
| Lead, . . . . .     | trace.                |
| Gold, . . . . .     | trace.                |
| Arsenic, . . . . .  | trace.                |
| Antimony, . . . . . | trace.                |

This was ground fine enough to pass through a 60-mesh screen, and  $1\frac{1}{2}$  pounds of the finely-ground material placed in the cast-iron tray, and the tray introduced into the oven-furnace. The furnace was lighted, and the gas and blast so regulated as to cause the temperature to rise slowly. After the expiration of one hour, the temperature had reached  $325^{\circ}$  C. At this stage the sulphur of the matte began to burn off, and owing to the heat of this combustion the temperature rose rapidly. In fifteen minutes the degree of heat of the charge ranged from  $470^{\circ}$  C. underneath to  $535^{\circ}$  at the surface where the oxygen of the air supported the combustion of the sulphur. Continuous stirring was required at this stage to prevent fritting or caking of the particles of the upper layer of the charge. As the matte was stirred, the temperature rose slowly, and at the end of another hour the material was uniformly heated throughout to  $590^{\circ}$  C. Until now, the upper portions had been hotter than those below. By this time the major part of the sulphur had been oxidized, and the heat from this source began to decline, so that from this time on the temperature of the upper layer was less than that underneath. At the end of another half-hour the temperature had fallen considerably, and was brought up again only by turning on more gas and blast. The door of the furnace was closed a little later. The highest temperature attained during the four hours the matte was roasting was  $750^{\circ}$ , and this was attained only at the bottom layer of the matte next the pan, just before the gas was turned off. -

The operation was stopped at this stage while the matte had the composition shown in sample No. 7 of Table XIII., and continued next day. About  $\frac{1}{4}$  of the partially roasted matte was taken in a roasting-dish of Denver fire-clay and heated in a gas muffle-furnace. The furnace was heated to  $720^{\circ}$  C., and the dish and contents introduced. The mouth of the muffle was closed by a fire-clay door. In half an hour the temperature had risen to  $750^{\circ}$  C., and considerable sulphate still remained, as shown by sample No. 9. On removing the door and adjusting the flame so that the muffle did not cool down, a draught was established in the muffle, and heavy fumes of sulphuric anhydride appeared at the top of the flue, indicating a rapid dissociation of the copper sulphate in the furnace. At



the end of 20 minutes every trace of neutral sulphate of copper had disappeared (see sample No. 10.) There was seen to be a great increase in the rate of dissociation at any temperature with a strong draught through the muffle, over that with closed muffle. This corresponds to the phenomenon observed in connection with the dissociation experiments in the electric furnace. After all the sulphates of copper had been decomposed, the charge was heated to  $850^{\circ}$ , to determine whether any material loss in silver sulphate occurred below the temperature, to which it was found to be safe to heat the pure sulphate of silver in the experiments with the electric furnace.

Samples were taken at intervals of 15 to 30 minutes, and these were put into convenient receptacles, labeled, and set aside for analysis.

#### METHODS OF ANALYSIS.

##### *Soluble Sulphates of Iron and Copper.*

Each sample was analyzed for 1° sulphates of iron and copper which were soluble in water, 2° insoluble or basic sulphates, 3° silver sulphate, and 4° total copper. Total silver was determined in a few cases. To ascertain the amount of iron and copper sulphates soluble in boiling water, two grammes of the sample were weighed out on the analytical balance and added to 150 c.c. distilled water in a No. 3 lipped beaker. The contents of the beaker were heated on an iron plate to boiling and allowed to remain at that temperature for a few minutes. The solution was filtered into a No. 4 beaker and the residue washed by decantation several times with boiling water, which water served for washing the filter. To the clear solution was added a piece of sheet aluminum,  $2'' \times 2'' \times \frac{1}{16}''$ , and a few drops of sulphuric acid. The solution was boiled again on the hot plate until all the copper was precipitated and the ferric iron reduced to the ferrous condition. The color-test with ammonium-sulpho-cyanate served to indicate when no ferric salt remained. The solution was decanted through a filter and the precipitated copper washed thoroughly by decantation with hot water, the wash-water being passed through the filter to prevent the loss of any particles of copper poured off. The filtrate was titrated for iron with a standardized solution of potassium permanganate.

The copper in the beaker and on the aluminum plate was dissolved in dilute nitric acid. A few drops of the dilute acid were poured onto the particles of copper on the filter and allowed to pass into the vessel containing the dissolved copper, and the filter was thoroughly washed with distilled water. Ammonia was added in excess, and the blue solution titrated with a standardized potassium cyanide solution. The results of these analyses, given in percentage of the two grammes employed, are shown in columns 4 and 5 in Table XI.

TABLE XI.—*Direct Results of Analysis of Samples.*

| No. of Sample. | Time.         | Temperature. | Cu as $\text{CuSO}_4$ . | Fe as $\text{FeSO}_4$ . | Basic Sulphates.          | Silver Sulphate.                        |
|----------------|---------------|--------------|-------------------------|-------------------------|---------------------------|-----------------------------------------|
|                |               | Deg. C.      | Per cent.               | Per cent.               | Per cent. $\text{SO}_4$ . | Oz. per T. = Per cent. of Total Silver. |
| 1              | After 75 min. | 500-520      | 4.498                   | 0.374                   | None.                     | .....                                   |
| 2              | " 90 "        | 550-560      | 7.656                   | 0.580                   | 1.066                     | .....                                   |
| 3              | " 105 "       | 565-570      | 8.900                   | 0.610                   | 2.542                     | .....                                   |
| 4              | " 120 "       | 585-595      | 10.144                  | 0.410                   | 4.305                     | trace.                                  |
| 5              | " 140 "       | 625-640      | 11.293                  | 0.403                   | 7.298                     | 20.                                     |
| 6              | " 190 "       | 655-675      | 11.627                  | 0.255                   | 8.534                     | 40.3                                    |
| 7              | " 235 "       | 720-750      | 9.057                   | trace.                  | 11.603                    | 55.1                                    |
| 8              | " 245 "       | 740-750      | 5.574                   | None.                   | 8.364                     | 70.                                     |
| 9              | " 265 "       | 750-760      | 4.115                   | .....                   | 6.068                     | 80.                                     |
| 10             | " 310 "       | 770-780      | None.                   | .....                   | 1.213                     | 90.2                                    |
| 11             | " 320 "       | 750-760      | .....                   | .....                   | None.                     | 92.8                                    |
| 12             | " 340 "       | 850          | .....                   | .....                   | None.                     | 90.4                                    |

The residues from all the samples except the last two, after treatment with boiling water, were of a decided green tinge, owing to the presence of particles of hydrated basic sulphate of copper,\* which is of a green color. Portions of the residues were heated in a porcelain crucible in the electric furnace, and after dehydration the basic salts were found to commence to decompose by heat alone at  $700^\circ \text{C}$ . This temperature corresponds with that at which the basic sulphate  $\text{CuO}, \text{CuSO}_4$  decomposes.

To determine the amount of basic sulphates present, the method used by Steinbeck† was employed. To the residue from the two grammes taken for the previous analyses was added three times its weight of sodium bicarbonate ( $\text{NaHCO}_3$ )

\* *Watt's Dictionary of Chemistry*, Muir & Morley (1894).

† *Chemische-Analytische Untersuchungen*, etc. Also Roscoe & Sch., vol. ii., pt. i. p. 339.

and enough water to dissolve most of the soda. This was allowed to stand for twenty-four hours with occasional shaking. The solution was filtered and the residue washed by decantation and finally on the filter, to remove every trace of dissolved sulphate. This solution was acidified with hydrochloric acid and the carbon dioxid removed by boiling. Barium chlorid was added in slight excess, and the whole was boiled a few minutes and set aside for twelve to twenty hours. The barium sulphate was determined gravimetrically, and from this the percentage  $\text{SO}_4$  from the basic sulphate in the sample calculated. Table XI. gives, in percentage of the two grammes of sample originally taken, the  $\text{SO}_4$  obtained by this method. The method is similar to the one given by Fresenius for the determination of lead sulphate. It was adapted by Steinbeck to ascertaining basic sulphates in samples from roasting matte. By careful tests he found that the sodium bicarbonate reacted with all the sulphate present, and had no effect on the sulphides.

#### *Analysis for Silver Sulphate.*

For silver sulphate determinations, 0.2 assay ton from each sample was taken and treated with hot water in a similar manner to that employed for the other soluble sulphates. If the copper in the solution amounted to more than 1 to 2 per cent. of the quantity of matte taken, the following method was employed: \* To the solution of sulphates was added sodium chlorid of about "normal" strength, to precipitate the silver as chlorid. Lead acetate and sulphuric acid were added to form a heavy precipitate to carry down the silver chlorid. The whole was allowed to stand for six to twelve hours, when the clear liquid was decanted through a filter, and finally the precipitate was removed to the same filter. The precipitate was scorified and cupelled for silver.

If the amount of copper present was less than 1 per cent., the silver in the hot-water solution was determined by titration with standardized ammonium sulpho-cyanate solution according to "Volhard's method." †

The silver insoluble in hot water was ascertained by treating

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\* *Manual of Practical Assaying*, Furman, pp. 250-251.

† Liebig's *Ann d. Chem.*, etc., 1. Sutton, *Volumetric Analysis*, 8th ed., p. 155.



the residue from the solution containing the silver sulphate with strong nitric acid and allowing the solution to stand on the hot plate until the red fumes were driven off. The silver was gotten by the combination method as given by Furman.\* The silver obtained from the residue was added to that from the hot-water solution, to give the total silver in any sample. In Table XI. the silver-content is given in ounces per ton, and since the original matte contain 100 oz. to the ton the figures in column headed "Silver Sulphate" represent also the percentage of total silver.

### *Reducing Factors.*

The data in Table XI. is not in a condition for direct comparison of the quantities of the sulphates at the various steps in the process. During the roasting operation much oxygen of the air was taken up in the formation of sulphates without a corresponding loss in sulphur. The weight of the charge increased as the sulphates continued to rise in amount, and decreased as these compounds were decomposed. The volume also increased and diminished, as was readily seen within the tray in the furnace. In analyzing the samples taken at successive stages in the process, the same weight of each sample was taken. Because of the rapidly changing weight of the roasting-charge, the amount of copper, or iron, or silver sulphate in these equal weights of samples did not represent the relative amount of this compound in the charge at these stages in the process. To enable one to compare the analytical data in Table XI., it was necessary to ascertain quantitatively the change in weight of the roasting-charge.

The total amount of copper in the charge did not change during the operation. The amount determined in equal weights of the respective samples varied through considerable limits. From these varying percentages of copper present in the different samples the change in weight of the charge was ascertained. For a decrease in the percentage of copper an increase in the weight of the charge must have taken place, and for an increase in copper-content of a sample a diminution in the weight of the charge. In other words, the relative weights of the charge

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\* *Manual of Practical Assaying.*

at different stages are in inverse ratio to the copper-content of equal weights of samples taken at these stages. Table XIII. gives the percentage of copper present in each sample taken. Sample 7 shows the lowest percentage of copper. At the time this sample was taken, the weight of the charge was a maximum. Reference to Table XI. shows the maximum total sulphates in this sample (7).

Putting the weight of the original matte, before roasting commenced, as unity, we obtain the weight at any step in the operation, as follows:

1 : X :: 39.00 (per cent. Cu in Sample 7) : 50.8 (per cent. Cu in original matte).

$X = 1.303$ , which is the ratio of the weight of the charge at the time Sample 7 was taken to the weight before roasting commenced. Table XII. gives such a ratio or "reducing factor" for each sample.

TABLE XII.—*Total Copper and Reducing Factor.*

| No. of Sample.  | Total Copper. | Inverse Ratio or Reducing Factor. |
|-----------------|---------------|-----------------------------------|
|                 | Per cent.     |                                   |
| Original Matte. | 50.80         | 1.000                             |
| 1               | 47.04         | 1.08                              |
| 2               | 44.17         | 1.15                              |
| 3               | 43.42         | 1.17                              |
| 4               | 42.70         | 1.19                              |
| 5               | 41.30         | 1.23                              |
| 6               | 40.64         | 1.25                              |
| 7               | 39.00         | 1.30                              |
| 8               | 44.58         | 1.14                              |
| 9               | 46.19         | 1.10                              |
| 10              | 50.78         | 1.00                              |
| 11              | 50.28         | 0.99                              |
| 12              | 50.29         | 0.99                              |

By the aid of these "reducing factors" the data of Table XI. may be brought into a condition for direct comparison. By multiplying the percentages of the different sulphates in each sample, as obtained by analysis, by the reducing factor for that sample, one obtains percentages which represent the relative amounts of these sulphates in the entire charge at the time the sample was taken. A table of corrected results may thus be obtained.

## TOTAL COPPER.

One gramme of each sample was treated with 7 c.c. nitric acid and 5 c.c. sulphuric acid in a flat-bottomed flask of 400 c.c. capacity. This was heated until the nitric acid was expelled and the sulphuric acid was boiling freely, then cooled and diluted with 50 c.c. distilled water. Ammonia was added in excess, and the solution transferred to a 500 c.c. flask, and further diluted to exactly 500 c.c. The flask and contents were allowed to stand until the precipitate of hydroxide of iron had subsided. The time required was from two to five minutes. By means of a pipette, an aliquot part of the blue solution, free from the brown precipitate, was taken out and titrated for copper with standardized potassium cyanide. This method was much shorter than the one ordinarily employed, wherein the copper is removed from the solution containing the iron and copper salts by means of metallic zinc or aluminum. The results from the two methods were found to check very closely. Comparative results on the hot-water solution of some of the samples are given below:

TABLE XIII—*Soluble Copper Sulphate.*

| Sample, . . . . .                 | No. 6.  | No. 7.  | No. 8.  | No. 10. |
|-----------------------------------|---------|---------|---------|---------|
|                                   | Per ct. | Per ct. | Per ct. | Per ct. |
| Aliquot part method, . . . . .    | 11.7    | 11.9    | 9.9     | 6.7     |
| Aluminum precipitation, . . . . . | 11.8    | 11.9    | 10.1    | 6.7     |

## DISCUSSION OF RESULTS OF ANALYSIS.

*Sulphates of Iron.*

Table XIV. gives the corrected results of analysis on twelve samples, taken at as many different stages of the process. At a temperature of about 350° C. the sulphur of the sulphides began to burn off, and the temperature rose rapidly until it reached a point near where the sulphate of iron is decomposed. The tendency to the formation of these sulphates would not be strong at a point so near the dissociation temperature. The small amount of the sulphate of iron shown in the table may be explained by this fact. The maximum amount of sulphate of iron present would not be sufficient to assist very materially in forming copper sulphate by the evolution of its sulphuric anhydride during dissociation, though it is explained by all the text-books that consider the Ziervogel process, that the copper



TABLE XIV.—*Corrected Results of Analysis of Samples.*

| No. of Sample. | Time.         | Temperature. | Cu as $\text{CuSO}_4$ . | Fe as $\text{FeSO}_4$ . | Basic Sulphates.          | Silver Sulphates. |
|----------------|---------------|--------------|-------------------------|-------------------------|---------------------------|-------------------|
|                |               | Deg. C.      | Per cent.               |                         | Per cent. $\text{SO}_4$ . |                   |
| 1              | After 75 min. | 500–520      | 4.858                   | 0.404                   | None.                     | .....             |
| 2              | “ 90 “        | 550–560      | 8.803                   | 0.67                    | 1.226                     | .....             |
| 3              | “ 105 “       | 565–570      | 10.413                  | 0.71                    | 2.974                     | .....             |
| 4              | “ 120 “       | 585–595      | 12.071                  | 0.49                    | 5.123                     | trace.            |
| 5              | “ 140 “       | 625–640      | 13.890                  | 0.49                    | 8.976                     | 25.               |
| 6              | “ 190 “       | 655–670      | 14.534                  | 0.32                    | 10.663                    | 50.4              |
| 7              | “ 235 “       | 720–750      | 11.774                  | None.                   | 15.084                    | 71.6              |
| 8              | “ 245 “       | 740–750      | 6.354                   | .....                   | 9.535                     | 79.8              |
| 9              | “ 265 “       | 750–760      | 4.526                   | .....                   | 6.675                     | 88.00             |
| 10             | “ 310 “       | 770–780      | None.                   | .....                   | 1.213                     | 90.20             |
| 11             | “ 320 “       | 750–760      | None.                   | .....                   | None.                     | 91.87             |
| 12             | “ 340 “       | 850          | None.                   | .....                   | .....                     | 89.50             |

sulphate is formed through the action of the sulphuric anhydride evolved from the decomposing sulphate of iron. To further ascertain if the iron sulphates played any particular rôle in the formation of copper sulphate, a matte containing no iron was prepared and roasted in the manner described above. The rapid accumulation of copper sulphate at temperatures corresponding to those at which this compound appeared in the iron-copper matte showed that the iron sulphates were not essential to the operation of sulphatizing the copper compounds. The rise in the sulphate of copper is a gradual one, and is not dependent on the action of the gaseous products of the dissociation of the sulphates of iron.

The maximum soluble iron sulphate was obtained in sample 3, taken at a temperature of  $570^\circ$ , immediately below that at which ferrous sulphate begins to decompose (*viz.*,  $590^\circ \text{C.}$ ). These sulphates decreased from this time until, at a temperature of  $700^\circ \text{C.}$ , only a trace remained.

#### *Soluble Sulphate of Copper.*

The soluble sulphate of copper reached its maximum at a temperature—measured with the contact of the couple below the upper layer—slightly above that at which its dissociation begins. The surface of the roast at this stage (sample 6) was cooler than the layers underneath the surface; and, while the dissociation had begun below the surface, because of its high temperature, the upper layer, where the sulphates really formed, had not reached the decomposing point, and was supplying the

material that was dissociating underneath. At temperatures near  $655^{\circ}$  C.—that at which the neutral sulphate commences to decompose—the change in amount of neutral sulphate was not rapid.

After sample 6 was taken the operation was carried on with the furnace-door closed, in order to keep the temperature as uniform as possible, and the gaseous products of dissociation were not readily removed. The result was that the dissociation was slow, though it was continuous, and at a temperature of  $750^{\circ}$  to  $760^{\circ}$  (sample 9) some 4 per cent. of the soluble sulphate remained. Fifteen minutes after sample 9 was taken, when the door of the muffle-furnace was opened and a strong draught established, the rate of dissociation was greatly increased. Inside of twenty minutes after the door was opened no soluble copper sulphate remained, as shown by sample 10.

#### *Basic Copper Sulphate.*

The basic copper sulphate results not alone from the decomposition of the neutral sulphate, but also from the action of the sulphides and sulphur dioxid on the sulphatizing roast.\* It appeared as a trace in sample 2, and increased in amount from that time until it reached a maximum in sample 7. The temperature at the time sample 7 was taken was somewhat above that at which the basic salt ( $\text{CuO}, \text{CuSO}_4$ ) begins to dissociate. The fact that the surface was cooler than the temperature indicated by the pyrometer may account for this apparent discrepancy; but, as has been shown on page —, if the neutral sulphate present is decomposing with the evolution of sulphuric anhydride, the dissociation of the basic salt may not begin until a temperature a few degrees above  $700^{\circ}$  C. is reached. The results in the oven and muffle-furnaces with the roasting matte confirm those obtained in the electric furnace. The diminution in amount of basic sulphate is continuous from the time of sample 7. Rapid action is shown by the table to have occurred when the furnace-door was opened—between the samples 9 and 10.

#### *Sulphate of Silver.*

No sulphate of silver was found in samples 1, 2, and 3, and but a faint trace in 4. From that time on, the amount increased

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\* Steinbeck, *Chem.-Anal.*, etc., p. 54.

until sample 11 was taken, at a temperature slightly above  $750^{\circ}$ , when the maximum was shown. No trace of either neutral or basic sulphate of copper remained in sample 11. The roasted matte was finally heated to  $850^{\circ}$  C., to determine whether the temperature could be safely raised to that point, as was shown to be true in the electric furnace. In this particular roast there was no necessity for proceeding beyond the time of sample 11, since, at that time, there remained no sulphates of copper to decompose. The loss due to the excessive heat was small, as seen by comparing the silver sulphate in samples 11 and 12.

The whole time occupied in the operation was 5 hours and 40 minutes: One hour in heating the furnace and matte to  $350^{\circ}$ , two hours and twenty minutes in forming sulphates, two hours in decomposing the sulphates of copper, and twenty minutes in heating to  $850^{\circ}$  C. after all the copper sulphates had disappeared.

#### RESULTS OF ROAST No. 2.

Another roast of one and a half pounds of the same matte was carried through, and the entire operation effected in the oven furnace. The temperature was raised more rapidly than in the former case, and the time during which the roasting proceeded was but three hours and ten minutes, a little more than half the time occupied in the previous operation. The roasting was completed in one operation. Two hours were taken to form sulphates, and these corresponded in amount to the similar compounds formed in the previous roast. Less than one hour was required to decompose the copper sulphates, the temperature during the dissociation period being much higher than it was during the same period in the former operation. Care was taken, however, not to heat the matte above  $850^{\circ}$  C. After all the copper sulphates had disappeared the charge was heated above  $850^{\circ}$  C. for fifteen minutes, the highest point reached being  $910^{\circ}$  C. The maximum silver sulphate occurred in sample 11 at  $835^{\circ}$ – $845^{\circ}$  C. This decreased rapidly after  $850^{\circ}$ – $860^{\circ}$  C. was attained; and in sample 13, taken at  $910^{\circ}$  C., the soluble silver compound amounted to less than one-half of that soluble at  $845^{\circ}$  C. in sample 11. Table XV. gives the direct results of the analyses of samples from this roast. Total copper and the reducing factors are shown in Table XVI., and the corrected results of analyses in Table XVII.

TABLE XV.—*Direct Results of Analysis of Samples.*

| No. of Sample. | Time.         | Temperature. | Cu as CuSO <sub>4</sub> . | Fe as FeSO <sub>4</sub> . | Basic Sulphates.            | Silver. Oz. per Ton. |
|----------------|---------------|--------------|---------------------------|---------------------------|-----------------------------|----------------------|
|                |               | Deg. C.      | Per cent.                 | Per cent.                 | Per cent. SO <sub>4</sub> . |                      |
| 1              | After 30 min. | 450          | 6.2                       | 0.8                       | 3.21                        | .....                |
| 2              | " 45 "        | 560          | 9.4                       | 0.8                       | 4.88                        | .....                |
| 3              | " 80 "        | 630          | 10.9                      | 0.5                       | 6.21                        | .....                |
| 4              | " 90 "        | 650          | 11.2                      | 0.45                      | 7.72                        | trace.               |
| 5              | " 100 "       | 670          | 11.4                      | 0.3                       | 12.23                       | trace.               |
| 6              | " 110 "       | 680          | 11.7                      | 0.26                      | 15.12                       | 26.25                |
| 7              | " 130 "       | 735-750      | 10.1                      | 0.13                      | 12.48                       | 38.14                |
| 8              | " 140 "       | 785-795      | 8.6                       | trace.                    | 11.68                       | 54.25                |
| 9              | " 150 "       | 800-810      | 6.5                       | None.                     | 10.52                       | 67.68                |
| 10             | " 160 "       | 815-830      | 4.5                       | .....                     | 8.51                        | 79.0                 |
| 11             | " 165 "       | 835-845      | 2.1                       | .....                     | 1.44                        | 90.0                 |
| 12             | " 175 "       | 855-870      | None.                     | .....                     | trace.                      | 77.2                 |
| 13             | " 190 "       | 910          | None.                     | .....                     | None.                       | 43.2                 |

TABLE XVI.—*Total Copper and Reducing Factors.*

| No. of Sample.  | Total Copper. | Reducing Factor. |
|-----------------|---------------|------------------|
|                 | Per cent.     |                  |
| Original Matte. | 50.8          | 1.000            |
| 1               | 44.4          | 1.14             |
| 2               | 43.3          | 1.17             |
| 3               | 42.8          | 1.19             |
| 4               | 41.2          | 1.23             |
| 5               | 40.6          | 1.25             |
| 6               | 38.5          | 1.32             |
| 7               | 38.8          | 1.30             |
| 8               | 39.0          | 1.29             |
| 9               | 39.4          | 1.28             |
| 10              | 44.5          | 1.14             |
| 11              | 49.5          | 1.01             |
| 12              | 51.4          | 0.99             |
| 13              | 51.4          | 0.99             |

TABLE XVII.—*Corrected Results of Analysis of Samples.*

| No. of Sample. | Time.         | Temperature. | Cu as CuSO <sub>4</sub> . | Fe as FeSO <sub>4</sub> . | Basic Sulphates. | Silver oz. per Ton = Per ct. |
|----------------|---------------|--------------|---------------------------|---------------------------|------------------|------------------------------|
|                |               | Deg. C.      | Per cent.                 | Per cent.                 | Per cent.        |                              |
| 1              | After 30 min. | 450          | 7.07                      | 0.91                      | 3.65             | .....                        |
| 2              | " 45 "        | 560          | 10.99                     | 0.94                      | 5.71             | .....                        |
| 3              | " 80 "        | 630          | 12.97                     | 0.59                      | 7.39             | .....                        |
| 4              | " 90 "        | 650          | 13.77                     | 0.55                      | 9.49             | .....                        |
| 5              | " 100 "       | 670          | 14.25                     | 0.37                      | 15.29            | trace.                       |
| 6              | " 110 "       | 680-690      | 15.44                     | 0.34                      | 19.96            | 34.65                        |
| 7              | " 130 "       | 735-750      | 13.13                     | 0.17                      | 16.22            | 49.58                        |
| 8              | " 140 "       | 785-795      | 11.09                     | trace.                    | 14.07            | 69.48                        |
| 9              | " 150 "       | 800-810      | 8.32                      | .....                     | 13.46            | 86.63                        |
| 10             | " 160 "       | 815-830      | 5.03                      | .....                     | 9.81             | 90.06                        |
| 11             | " 165 "       | 835-845      | 2.12                      | .....                     | 1.45             | 90.90                        |
| 12             | " 175 "       | 855-870      | None.                     | .....                     | trace.           | 76.42                        |
| 13             | " 190 "       | 910          | None.                     | .....                     | None.            | 42.76                        |



*Basic Sulphate of Copper.*

The basic sulphate of copper is practically insoluble in distilled water, hot or cold; but in water containing neutral copper sulphate in solution this basic salt is soluble to a considerable degree. This fact partly accounts for the maximum soluble sulphate coming at a temperature above that at which the neutral sulphate begins to decompose (viz.,  $653^{\circ}$  C.). The basic salt increases rapidly from the time the temperature of dissociation of the neutral salt is reached (sample 4); and the solution of neutral sulphate, acting upon this increased quantity of basic sulphate, gives the maximum soluble sulphate at a stage when the actual amount of neutral salt in the roasting mass has passed its maximum. This explanation applies to the other roasts, whose analyses are given in this paper.

## ROASTING OF MATTE FREE FROM IRON.

Copper sulphide was prepared by treating a solution of copper sulphate with hydrogen sulphide from a generator. The sulphide was collected and dried. To 175 grammes of this black sulphide was added a small quantity of silver sulphide, prepared by precipitation from a solution of silver nitrate. These sulphides were mixed and added to a fire-clay crucible, and fused in a gas crucible furnace. The molten matte was poured into cold water contained in an earthen jar of 5 gallons capacity. The granulated mass was ground in a mortar to pass through a 60-mesh screen. The silver and copper contents were as follows: Copper, 74.8 per cent.; silver, 235 oz. to the ton. One hundred grammes of this matte was placed in a fire-clay roasting-dish and heated in the muffle-furnace. The couple of the pyrometer was placed within the roasting-charge. Though but forty minutes was occupied in reaching the temperature of maximum copper sulphates, and no iron sulphate was present to assist in forming these compounds, still the amount formed, as shown in sample 1, was considerable. Table XVIII. gives the corrected results of analyses of samples taken at successive stages in the process. The results of this roast on copper matte free from iron correspond with those of the iron-copper matte given in Tables XIV. and XVII.

In the operation of roasting the argentiferous copper mattes

TABLE XVIII.—*Corrected Results of Analysis of Samples*

| No. of Sample.    | Time. | Temper-<br>ature. | Total<br>Copper. | Reduc-<br>ing Fac-<br>tor. | Cu as<br>CuSO <sub>4</sub> . | Basic<br>Sulphate.           | Silver<br>Sulphate. | Silver<br>Sulphate. | Total<br>Silver. |
|-------------------|-------|-------------------|------------------|----------------------------|------------------------------|------------------------------|---------------------|---------------------|------------------|
|                   |       | Deg. C.           | Per ct.          |                            | Per ct.<br>of whole          | Per ct.<br>SO <sub>4</sub> . | Oz. per<br>Ton.     | Per ct.             | Oz. per<br>Ton.  |
| Original Matte... |       |                   | 74.80            | 1.000                      |                              |                              |                     |                     |                  |
| 1 After 40 min.   |       | 675-685           | 65.13            | 1.147                      | 8.44                         |                              | trace               |                     | 235              |
| 2 " 70 "          |       | 750-760           | 66.58            | 1.123                      | 5.94                         | 11.66                        | 184.2               | 78.3                |                  |
| 3 " 87 "          |       | 790-800           | 67.12            | 1.114                      | 5.48                         | 10.57                        | 189.4               | 80.6                |                  |
| 4 " 97 "          |       | 810-815           | 69.53            | 1.076                      | 2.81                         | 4.12                         | 201.2               | 85.6                |                  |
| 5 " 107 "         |       | 845-850           | 75.00            | .998                       |                              | trace                        | 211.5               | 90.0                |                  |
| 6 " 117 "         |       | 870-875           | 77.31            | .967                       |                              |                              | 145.8               | 61.9                |                  |
| 7 " 130 "         |       | 890-900           | 77.30            | .967                       |                              |                              | 49.9                | 21.2                |                  |

it was found desirable to have an excess of air,\* not only to facilitate the production of sulphates, but also for the removal of the gaseous products of their decomposition. The more rapid the dissociation, the less the time during which the roasting matte is held at a high temperature, and consequently the less the loss in silver. Above 655° C. the sulphate of silver is in the liquid state, and experiments seem to indicate a slow but continuous loss—possibly by volatilization as sulphate—after the substance is thoroughly fused, even though the temperature is not raised to the point at which it decomposes.

On the whole, the results of the roasting operation confirmed the facts determined with the electric furnace. To decompose the sulphates of copper, a temperature above 700° C. was required. The rate of decomposition of the sulphates was more rapid as the temperature was raised above 700° C.; but there was found to be no necessity for heating the charge above 800° C. to complete the process. Care needed to be taken not to allow the furnace in any part to become heated above 850° C.

By the aid of a reliable pyrometer, and with a range of 150° C. (= 270° F.) between the temperature at which the basic sulphate of copper begins to change to copper oxid and that temperature to which silver sulphate can be safely heated, the workman in charge of the furnace should be able to conduct the operation of roasting, in the Ziervogel process, without undue loss of silver. Having in mind the facts set forth in this

\* "The Metallurgy of Argentiferous Compounds," by H. M. Howe, in *Production of Gold and Silver in the United States*, Burchard, 1883, p. 757.

paper, the superintendent should be able to get good results in the Ziervogel process without the aid of expensive skilled labor in the management of the roasting-furnace.

RESULPHATIZING THE METALLIC SILVER RESULTING FROM THE  
DECOMPOSITION OF THE SILVER SULPHATE BY  
EXCESSIVE HEATING.

The iron-copper matte of the composition, given on page , was roasted in the oven furnace until all the sulphates of iron and copper were decomposed. The temperature was allowed to rise to  $905^{\circ}\text{C}$ ., and, as a result, much of the silver sulphate was decomposed, with a corresponding precipitation of metallic silver. Analysis of the dead roasted charge showed but 35.2 per cent. of the entire silver to be soluble as sulphate.

A portion of this roasted material was mixed with 5 per cent. of its weight of dehydrated ferrous sulphate, and heated in a roasting-dish in the muffle-furnace for fifteen minutes. The temperature was allowed to rise slowly above  $590^{\circ}\text{C}$ ., and the highest point attained was  $750^{\circ}\text{C}$ .

0.6 A.T. of the material was weighed out, and the sulphate of silver dissolved by means of hot water, as already described. The solution was titrated for silver with ammonium-sulpho-cyanate of such strength that 1 c.c. corresponded to 0.0047 g. of silver. 11.6 c.c. of the solution was required, showing 0.0545 grammes of silver, soluble as sulphate, in the 0.6 A.T. of the roasted matte, or 90.8 oz. per ton.

The percentage of soluble sulphate was thus increased from 35.2 to 90.8 by means of the ferrous sulphate added to the charge.

A second experiment was taken through with a quantity of the same dead-roasted matte, containing 35.2 oz. silver per ton, soluble in hot water. A relatively larger amount of ferrous sulphate was added to the charge, and the roasting occupied more time. The results of the titration with ammonium-sulpho-cyanate showed 93.8 oz. silver per ton, soluble in hot water.

Another sample of the 100 oz. matte which had been dead-roasted, but which had been heated only to a temperature of  $880^{\circ}\text{C}$ . and contained 64.4 oz. silver soluble as sulphate, was heated in the same manner as described above. After the re-



sulphatizing by the ferrous sulphate, the percentage of silver soluble as sulphate had been raised from 64.4 to 91.3.

From these experiments it is seen that the metallic silver, in the finely-divided condition in which it exists in the over-roasted matte, is readily resulphatized by the sulphuric anhydride evolved from the decomposing ferrous sulphate. No doubt other decomposable sulphates would accomplish similar results, providing their dissociation occurs at a sufficiently low temperature. The sulphates of sodium and potassium, as such, do not readily decompose by heat alone. Ferrous sulphate is a convenient compound to employ, not only because of its comparative cheapness, but because it begins to decompose at a temperature far below that to which the sulphate of silver can be safely heated. Though it begins to decompose below  $600^{\circ}$  C., the decomposition is not rapid until  $650^{\circ}$  to  $700^{\circ}$  C. is attained. If the mixture of over-roasted matte and ferrous sulphate be rapidly heated to a temperature near  $700^{\circ}$  C.—*i.e.*, that at which the basic sulphate dissociates—there will be little cupric sulphate formed, but the sulphuric anhydride fumes will react directly upon the metallic silver. There will, therefore, be no necessity for raising the temperature or prolonging the time in order to decompose the sulphates of copper, and thereby running the risk of again depositing the silver of the sulphate in the metallic state.

#### BIOGRAPHICAL.

Robert Henry Bradford was born in Salt Lake county, Utah, in the year 1871. He attended the public school in district No. 25 in his native county, and the Normal School of the University of Deseret (now University of Utah), receiving his normal diploma in 1890. He was principal of one of the public schools in Salt Lake City for two years; then entered the University of Utah, from which he received the degree of B.S. in 1895. He studied at the University of Chicago during the summers of 1895 and 1896. Was appointed instructor in the University of Utah in 1895, which position he held until 1898, when he was made Assistant Professor of Mineralogy and Metallurgy. In July, 1900, he received leave of absence to attend Columbia University, where he was Fellow in Metallurgy for two years (1900–1902), during which time he pursued metallurgy as his major subject, and mining and mineralogy as minors.









